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(54) Title: THE USE OF SURFACTANTS AS PLASTICIZERS TO REDUCE VOLATILE ORGANIC COMPOUNDS IN WATER-BASED POLYMER COATING COMPOSITIONS (57) Abstract The invention relates to an improved water-based polymer coating composition comprising a polymer resin, water and surfactant. As an improvement over prior water-based polymer coating compositions an anionic and/or nonionic surfactant is present in an amount effective to plasticize the coating formed from the composition. A water-based polymer coating composition of the invention is also substantially free from cosolvents. The invention also relates to a method of coating a substrate and a substrate which has been coated with a coating formulation of the invention.		

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**THE USE OF SURFACTANTS AS PLASTICIZERS TO REDUCE
VOLATILE ORGANIC COMPOUNDS IN WATER-BASED
POLYMER COATING COMPOSITIONS**

FIELD OF THE INVENTION

The invention relates to the use of surfactants as plasticizers in water-based polymer coating compositions to reduce or eliminate the need for conventional cosolvents and to reduce the overall volatile organic compounds (VOC's) of the coating
5 composition.

BACKGROUND OF THE INVENTION

Both legislative and marketplace developments are pushing for reduced volatile organic emissions in a variety of industries. In an increasing number of industries,
10 aqueous coating compositions continue to replace solvent-based coating compositions in efforts to significantly reduce volatile organic emissions. A variety of paints, inks, sealants and adhesives, for example, which were previously formulated with organic solvents are now formulated as aqueous compositions. Emissions from coatings compositions commonly result from volatile organic compounds (VOC's) in the
15 compositions. The amounts of VOC's in a coating composition are expressed in grams per liter (g/l).

While the move from organic solvent-based to aqueous compositions brings environmental, safety and health benefits, aqueous coating compositions must still meet or exceed the performance standards expected from solvent-based coating compositions.
20 The coatings or films must form at ambient temperatures (35° to 160°F), yet have good performance properties after curing. For example, a coating composition should exhibit good print and block resistance and yield good adhesion and tensile properties. Once cured, most applications require that the coating be unaffected by environmental conditions such as water, humidity, and end-use temperature fluctuations.

25 Aqueous coating compositions may contain upwards of ten to twenty components which are generally identified by their function. For example, in addition to a resin or resins (also called latexes or binders), an aqueous coating composition may have

pigments, extenders, antisetling agents, dispersants, surfactants (such as wetting agents, defoamers, and antifoamer), rheology modifiers, coalescing solvents, plasticizers, water, glycols, catalysts, biocides, crosslinkers, and colorants. Glycols are components added for freeze-thaw resistance, wet edge properties and as aids in low temperature

5 coalescence. Representative glycols used for these purposes include ethylene glycol and propylene glycol. Because the glycols generally evaporate at ambient conditions, they contribute to VOC's found in aqueous coating formulations. A typical contribution to VOC's by glycols would be 100 to 200 grams per liter. Glycols are one of the first components aqueous coating manufacturers seek to decrease or eliminate in an effort to
10 reduce emissions. However, the resulting coating may then suffer in the desired properties of low temperature coalescence, freeze/thaw resistance and wet edge.

Cosolvents (also known as coalescing solvents) are commonly employed in aqueous compositions to aid in film formation (or knitting-together) of hard latex particles. This hardness can be measured in terms of the starting film-formation
15 temperature or of the glass transition temperature of the manufactured latex solid. As drying occurs, the cosolvents evaporate from the coating and the glass transition temperature of the coating approaches that of the starting resin. The addition of cosolvents enables the coating to behave like a softer film-forming material during drying and then perform as a harder, resistant film after drying. Examples of cosolvents include
20 aliphatic and aromatic hydrocarbons and oxygenated solvents, such as alcohols, ketones and glycol ethers. A typical amount of cosolvent ranges from 50 to 300 or more grams per liter of coating composition. Coating compositions based on cosolvents are described, for example, in *Paint Handbook*, 1-12 to 1-24 (Harold B. Crawford & Beatrice E. Eckes eds., 1981), incorporated here by reference. Because cosolvents present in the
25 coating formulation contribute considerably to VOC's content and tend to contribute odor to the coating, cosolvents are becoming more undesirable in aqueous coatings. However, in many aqueous coating systems, the elimination of the cosolvent(s) result in either lack of film formation or such poor film formation that the coating has poor appearance and poor resistance properties. In some cases, plasticizers may be added to the aqueous
30 coating formulation to replace some or all of the cosolvents. Typically, plasticizers are

organic compounds that do not significantly evaporate at ambient conditions but remain in the coating. Examples of typical plasticizers would be chemicals from the phthalate, adipate, and benzoate families. They soften the polymer and are used to impart flexibility to an otherwise hard and brittle polymer. However, plasticizers, especially at high levels, can have deleterious effects on coating performance properties. Because the coating remains soft, it can have poor block and print resistance, poor stain resistance and a tacky feel.

Many of the components discussed above used to formulate waterborne coatings have small amounts of volatile compounds present along with the components. Some examples are the solvents that colorants are dispersed in, the solvents that catalysts are dispersed in, and even the glycols or solvents that are present in many commercial surfactants, biocides, defoamers, or rheology modifiers. For example, the low level of VOC calculated for the formulation used in Examples 1-6 below (11 g/l) arises from a particular component; the solvents present in the cobalt catalyst employed.

Surfactants are commonly used in coating formulations to improve wetting of the substrate by the coating, and wetting of the pigment by the resin. They can also improve formulating latitude by preventing shocking of the coating composition as various components are added and can increase the service life of the coating by increasing shelf stability. Typically, low levels of surfactants are used to accomplish these goals and mixtures of surfactants may be employed to impart one or more of the properties listed above. Surfactants are not generally volatile materials under ambient conditions and remain in the coating during the drying process. However, at the low concentrations typically used, little effect on polymer hardness or coating performance is observed. If too much surfactant is used in the aqueous coating composition, the wet coating could exhibit excessive foaming and poor thickening efficiency with thickeners while the cured coating could have problems with water sensitivity, poor exterior durability and poor block, stain and print resistance. Thus, surfactants are typically used in the lowest amounts necessary to achieve their beneficial properties while avoiding any detrimental effects.

A discussed above, a need exists to reduce or eliminate VOC's from aqueous coating compositions without effecting wet coating or end-use performance properties. The invention answers that need.

5 SUMMARY OF THE INVENTION

It has been discovered that surfactants can be employed at levels similar to those used by conventional cosolvents and function as a plasticizers in the coating, thus eliminating the need for conventional cosolvents and eliminate the VOC's associated with the cosolvents. Preferred surfactants of the invention can be used to plasticize the
10 coating, aid in low temperature film formation and contribute to the typical properties associated with surfactants in coatings while not contributing deleteriously to the final balance of properties in the finished coating.

The invention relates to an improved water-based polymer coating composition comprising a polymer resin, water and surfactant. As an improvement over previous
15 water-based polymer coating compositions an anionic and/or nonionic surfactant is present in an amount effective to plasticize the coating formed from the composition. A water-based polymer coating composition of the invention is also substantially free from cosolvents. The invention also relates to a method of coating a substrate and a substrate which has been coated with a coating formulation of the invention.

20

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to an improved water-based polymer coating composition comprising a polymer resin, water and surfactant. An anionic and/or nonionic surfactant is present in an amount effective to plasticize the coating formed from the composition.
25 This improves prior water-based coating compositions by reducing or eliminating the cosolvent and reducing the amount of VOC's in the coating composition. A water-based polymer coating composition of the invention is also substantially free from cosolvents. Preferably, the VOC of the coating is less than 250 g/l, more preferably less than 50g/l, even more preferably less than 25 g/l and most preferably VOC's are eliminated.

Aqueous emulsion polymers or latexes in both clear and pigmented form are well-known. Examples of their uses include interior and exterior architectural coatings, general metal coatings, adhesives, and the like. Examples include the aqueous coating compositions described in *Technology of Paints, Varnishes and Lacquers*, Robert E.

5 Krieger Publishing Co., Huntington, NY 1974, U.S. Patent Nos. 5,002,998 and 5,185,397 and in GB Patent No. 2,206,591, all of which are incorporated here by reference. Water-based polymer coating compositions conventionally contain from about 10 to about 40% by volume of solids.

Synthetic latexes are well known and can be made by emulsion polymerization
10 techniques from styrene-butadiene copolymer, acrylate resins, polyvinyl acetate, and similar materials. For example, latexes can be formed by aqueous emulsion polymerization of ethylenically unsaturated monomers such as styrene, butyl acrylate, methyl methacrylate, vinyl acetate, vinyl 2-ethylhexanoate, acrylic acid, acrylonitrile, glycidyl methacrylate, 2-hydroxyethyl acrylate and the like. Preferred latexes for use in
15 the invention include those described in U.S. Patent No. 5,539,073 and copending applications Serial Nos. 08/861,431; 08/061,433; 60/047,324; 08/861,437; 08/861,436, all of which are incorporated here by reference.

Water-based polymer coating compositions may comprise pigments (organic or inorganic) and/or other additives and fillers known in the art. For example, a latex paint
20 composition may comprise a pigment and one or more additives or fillers used in latex paints. Such additives or fillers include, but are not limited to, leveling, rheology, and flow control agents such as silicones, fluorocarbons, urethanes, or cellulose; extenders; curing agents such as multifunctional isocyanates, multifunctional carbonates, multifunctional epoxides, or multifunctional acrylates; reactive coalescing aids such as
25 those described in U.S. Patent No. 5,349,026 (which are incorporated here by reference); flattening agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; extenders; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents;
30 plasticizers; reactive plasticizers; drying agents; catalysts; crosslinking agents; or

coalescing agents. Specific examples of such additives can be found in Raw Materials Index, (published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, NW, Washington, D.C. 20005), which is incorporated here by reference.

As discussed above, low levels of surfactants have conventionally been used in water-based polymer coating composition for their surfactant properties.

Advantageously, it has been discovered that surfactants can be employed at levels similar to those of conventional cosolvents and function as plasticizers in the coating. This eliminates the need for conventional cosolvents and significantly reduces, or preferably eliminates, the VOC's in the coating composition, particularly VOC's associated with the cosolvents. Further, problems such as blocking, poor print and stain resistance associated with plasticizers, are eliminated.

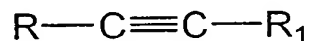
Any anionic or nonionic surfactant, as well as mixtures, may be used in a water-based polymer coating composition of the invention. The surfactant is present in an amount effective to plasticize a coating formed from the composition, preferably ranging from about 3 to about 10% by weight of the dry polymer. Preferred anionic surfactants include alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates. More preferably, the anionic surfactant is selected from sodium lauryl sulfate, sodium octylphenol glycolether sulfate, sodium dodecylbenzene sulfonate, sodium lauryldiglycol sulfate, ammonium tritertiarybutyl phenol and penta- and octa-glycol sulfonates, sulfosuccinate salts such as disodium ethoxylated nonylphenol half ester of sulfosuccinic acid, disodium n-octyldecyl sulfosuccinate, sodium dioctyl sulfosuccinate, and mixtures thereof. AEROSOL 18 surfactant, a 35% solution of disodium N-octyldecyl sulfosuccinimate in water and AEROSOL OT-75 surfactant, a 75% solution of sodium dioctyl sulfosuccinate in water, both available from Cytec Industries, Inc. are preferred anionic surfactants.

Preferably the nonionic surfactant is a polyether nonionic surfactant, more preferably, an alkyl polyglycol ether, an alkyl phenol polyglycol ether or a mixture thereof, such as those disclosed in U.S. Patent Nos. 4,912,157 and 5,554,675 the disclosure of which are incorporated herein by reference. Preferred alkyl phenol polyglycol ethers include ethoxylation products of octylphenol, nonylphenol, diisopropyl

phenol, triisopropyl phenol or mixtures thereof. Preferred alkyl polyglycol ethers include ethoxylation products of lauryl alcohol, oleyl alcohol, stearyl alcohol or mixtures thereof. Preferred nonionic surfactants include the TERGITOL 15-S-40 and TERGITOL NP-40 surfactants available from Union Carbide. TERGITOL 15-S-40 surfactant (CAS # 68131-40-8) is a reaction product of a mixture of 11-15 carbon, linear secondary alcohols and ethylene oxide. TERGITOL NP-40 surfactant is the reaction product of a nonylphenol and about 40 moles of ethylene oxide.

Most preferably the alkyl polyglycol ether is selected from compounds of the formula:

10



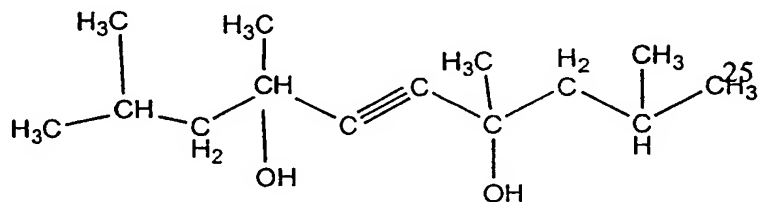
wherein R and R₁ are each selected from straight and branched alkyls having from 1 to 15 carbon atoms and wherein at least one of R and R₁ contains from 1 to 3 hydroxyl groups, and the H of each hydroxyl group is independently unsubstituted or substituted with a

15 substituent of the formula

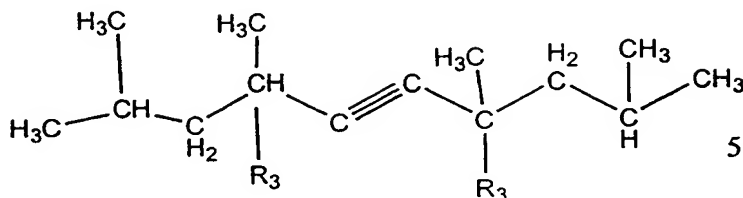


wherein n and m each range from 1 to about 50 and wherein the total of n and m is less than about 60. These compounds are known in the art and are available commercially from Air Products and Chemicals, Inc. under the trade name SURFYNOL®, including the SURFYNOL® 104 series, SURFYNOL® 420, 440, 465 and 485, also known as the SURFYNOL® 400 series.

SURFYNOL® 104 has the following formula:



The SURFYNOL® 400 series have the following general formula:



wherein R_3 is $(\text{CH}_2-\text{CH}_2-\text{O})_n\text{H}$ and wherein n is a number ranging from 1 to 30, with SURFYNOL® 420 having 1.3 moles of ethylene oxide, SURFYNOL® 440 having 3.5 moles of ethylene oxide, SURFYNOL® 465 having 10 moles of ethylene oxide and

10 SURFYNOL® 485 having 30 moles of ethylene oxide.

Upon formulation, a coating formulation of the invention containing a polymer or waterborne polymer composition may then be applied to a variety of surfaces, substrates, or articles, *e.g.*, paper, plastic, steel, aluminum, wood, gypsum board, concrete, brick, masonry, or galvanized sheeting (either primed or unprimed). The type of surface,

15 substrate, or article to be coated generally determines the type of coating formulation used. The coating formulation may be applied using means known in the art. For example, a coating formulation may be applied by spraying, brushing, rolling or any other application method to coat a substrate. In general, the coating may be dried by heating but preferably is allowed to air dry. Advantageously, a coating employing a

20 polymer of the invention may be thermally or ambiently cured. As a further aspect, the invention relates to a shaped or formed article which has been coated with a coating formulation of the invention.

The following examples are intended to illustrate, not limit, the invention. The examples of various coating compositions of the invention use the following materials

25 not described above:

TAMOL 1124 is a dispersant sold by Rohm and Haas.

ROPAQUE OP-62LO is an opaque polymer sold by Rohm and Haas.

ACRYSOL RM-5 is a rheology modifier (thickener) sold by Rohm and Haas.

COBALT HYDROCURE II (cobalt neodecanoate, 45% solids) is a cobalt drier

30 sold by Mooney Chemical, Inc., Cleveland, Ohio.

FOAMASTER AP and VF are defoamers sold by Henkel Corporation, Ambler, PA.

TRITON CF-10 is a surfactant sold by Union Carbide Chemicals and Plastics, Corp.

5 CELLOSIZ 4400 H is a rheology modifier sold by Union Carbide, Bound Brook, NJ.

DOWICIL 75 is a preservative sold by DOW Chemical Company, Midland, MI.

TI-PURE R-900, R-746 and R-760 are titanium dioxide pigments sold by Du Pont, Wilmington, DE.

10 OMYACARB UF is a calcium carbonate pigment, sold by Omya Inc., Proctor, Vermont.

RHEVOIS CR2 is a rheology modifier sold by Allied Colloids, Suffolk, Virginia.

TAFIGEL PUR 45 is a rheology modifier distributed by King Industries, Norwalk, CT.

15 TREM LF-40 is a polymerizable surfactant sold by Henkel Corporation, Ambler, PA.

HITENOL HS-20 is a polymerizable surfactant available from Daiichi Kogy Seiyaku.

POLYMIN-G is a poly(alkyl ethylenimine) available from the BASF Corporation.

20 TERGITOL 15-S-40 and TERGITOL NP-40 are surfactants available from Union Carbide Chemicals and Plastics, Corp.

AEROSOL 18 and AEROSOL OT-75 are anionic surfactants available from Cytec, Industries, Inc.

25 PROXEL GXL is a preservative sold by Zeneca Biocides, Wilmington, DE.

DURAMITE is a calcium carbonate pigment sold by ECC America, Atlanta, GA.

NYTAL 300 is a talc pigment sold by RT Vanderbilt, Norwalk, CT.

The following methods were used to evaluate the coatings prepared according to the invention.

Constant Temperature and Humidity Room:

Films were prepared and film measurements were conducted at ASTM standard conditions for laboratory testing of $73.5 \pm 3.5^{\circ}\text{F}$ ($23 \pm 2^{\circ}\text{C}$) and $50 \pm 5\%$ relative humidity.

5 Minimum Film Forming Temperature (MFFT):

Minimum film forming temperature (MFFT) is determined by casting a wet latex film with a 4-mil applicator on an MFFT bar set at a temperature range in which the film will coalesce during drying, visually observing the film on the MFFT bar after 30 minutes, and recording the temperature at which the film appears to have coalesced and is
10 free of cracks and film defects.

Tensile:

Tensile tests are performed in the CTH room on a on a United Tensile Tester, which has constant rate of elongation machine. Film samples are obtained by casting the sample on release paper with a 7 mil bird bar, drying the film for the desired time at the
15 stated conditions, and cutting a dogbone-shaped thin-film sample with a 1" wide die. The film is measured for film thickness, mounted in the tensile tester grips and tested at a cross head speed of 1"/minute using a 5 lb-force load cell. Ten samples are run and the five samples with the greater breaking stress are averaged for all tensile values reported according to ASTM

20 Glass Transition:

Onset and midpoint temperatures were determined on film samples using a differential scanning calorimeter (DSC) in a nitrogen atmosphere at heating rate of $20^{\circ}\text{C}/\text{minute}$. Values quoted are from the reheat curve.

Paint Viscosity:

25 Paint viscosity (in Krebs Units) was measured after 24 hours using a Krebs-Stormer viscometer.

Gloss:

Gloss was measured on 6 mil (wet) thick films cast on Leneta 2B opacity paper after 24 hours using a Micro-Tri-Glossmeter by BYK-Gardner according to ASTM
30 method D 523 Test Method for Specular Gloss.

Blocking Resistance:

Blocking resistance was determined using 6 mil (wet) films on Leneta 2B opacity paper according to ASTM 4946 Test Method for Blocking Resistance of Architectural Paints using 1 psi pressure after film dried to designated times. Heated block resistance
5 was determined in a forced air oven at 120°F with the painted surfaces face-to-face under 1 psi pressure for 30 minutes. The tests were numerically rated where a rating of 10 represents 100% pass where painted surfaces lift apart with no noise; a rating of 9-4 represents the degree of noise when painted surfaces are separated; a rating of 3-1 represents degree of destruction of the painted surfaces when the two surfaces are
10 separated; and a rating of 0 represents 100% fail where the painted surfaces flow completely together and complete destruction of the films occurs upon separation.

Print Resistance:

Print resistance was determined using 6 mil (wet) films on Leneta 2B opacity paper according to ASTM D 2064 - 91 Test Method for Print Resistance of Architectural
15 Paints using a 4 pound weight placed on top of a #6 black rubber stopper which was placed on four layers of cheesecloth after film dried to designated times. Heated print resistance was determined in a forced air oven at 120°F with folded cheesecloth (as above) under a pressure of 4 pounds for 30 minutes. The tests were numerically rated as per ASTM D2064-91.

20 Scrub Resistance:

Scrub resistance was determined following ASTM D2486 Test Method for Scrub Resistance of Architectural Coating. The coating is applied at 7 mil wet on Scrub Test Charts Form P121-10N and allowed to dry for the specified period of time. The panel is placed in a Gardco Scrub Machine, Model D-10V, 10 g of Standardized Scrub Medium
25 (abrasive type) for ASTM D2486 and D3450 is placed on the scrub brush, the panel is wet with 5 ml DI water, the test machine counter is zeroed, and the test is run at the maximum test speed on the machine. After each 400 cycles before failure, the brush is removed and 10 more g of scrub medium is added evenly on the bristles, the brush is replaced, 5 ml of DI water is placed on the panel and the test is continued. The test is run

to failure. Failure is defined as the number of cycles to remove the paint film fully in on continuous line across the width of the shim.

Wet Adhesion Test:

This procedure tests the coatings adhesion to an aged, alkyd substrate under wet, scrubbing conditions. This procedure is described in "VYNATE™ (Union Carbide Chemicals and Plastics Corporation) - Vinyl Emulsion Vehicles for Semigloss Interior Architectural Coatings," M. J. Collins, et. al., presented at the 19th Annual "Water-Borne High-Solids and Powder Coating Symposium", February 26-28, 1992, New Orleans, Louisiana, USA

10 A ten-mil drawdown of a commercial gloss alkyd paint is made on a "Leneta" scrub panel (adhesion varies from alkyd to alkyd - a Glidden Industrial Enamel was used.) The alkyd film is allowed to age one week at ambient conditions, then baked at 110°F for 24 hours, and then aged at least one more week at ambient conditions. A seven-mil drawdown of the test paint is then made over the aged alkyd and allowed to air
15 dry three days. (In order to differentiate between samples that pass this test, dry times may be shortened. Seven days is a common period, and occasionally 5 hours dry time is used. Constant temperature/humidity conditions, 72°F/50%, are normally used for drying.) The test paint is then cross-hatched with a razor and submerged in water for 30 minutes. The paint film is inspected for blistering and scratched with the fingernail to
20 gauge the adhesion. While still wet, the panel is placed on a "Gardner" scrub machine. Ten ml of five percent "LAVA™" soap slurry are added, and the Nylon scrub brush (WG 2000NB) is passed over the scored paint film area. Water is added as needed to keep the paint film wet (flooded). The number of brushing cycles for initial peel and ten percent peel are noted. The number of cycles for complete removal of the film is often noted
25 also.

Stain Test:

Apply test paint with 6 mil draw down bar. After draw down, allow the test paint(s) to cure for 21 days at 72°F ± 2 and relative humidity of 50% ± 2. Expose the paint film to black shoe polish, catsup, TOP JOB®, crayon, grape juice, red KOOL AID®
30 and PINE SOL® for a total time of 5 hours. Expose the paint film to mustard, coffee and

nigrosine for a total of 30 minutes. Expose the paint film to red ink and blank ink for a total of 5 minutes. Expose the paint film to iodine for 30 seconds. Cover all stains with 1½ inch watch glass for the specified exposure time. Remove the stain with a soft cloth soaked in a mild detergent solution. Rate the degree of stain using a scale of 1-5 with 1 =

5 no stain and 5 = extreme stain of film destroyed.

Low Temperature Coalescence:

Low temperature coalescence was determined in accordance with ASTM D3793-89.

10 EXAMPLES

The following polymer resins were prepared for use in the water-based polymer coating compositions of the invention:

RESIN A

To a 5 gallon resin kettle equipped with a condenser, nitrogen purge, and above
15 surface feed tube were added 4176.6 g of water, 57.55 g of sodium carbonate, 22.65 g of TREM LF-40 (40% solids in water), 10.82 g of TERGITOL NP-40 (70% solids in water), 138.3 g of methyl methacrylate, 228.4 g of styrene, 266.4 g of 2-ethylhexyl acrylate, and 1.3 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an
20 initiator charge composed of 60.8 g of sodium persulfate dissolved in 343.4 g of demineralized water were added to the reactor. An emulsified monomer mixture composed of 2597.7 g of water, 65.56 g of TREM LF-40, 57.2 g of TERGITOL NP-40, 849.5 g of methyl methacrylate, 1402.8 g of styrene, 1636.6 g of 2-ethylhexyl acrylate, and 7.8 g of trimethylolpropane triacrylate followed by 100 g line flush of demineralized
25 water, was fed over 125 minutes. Five minutes after the emulsion feed was begun, an initiator solution composed of 34.3 g of sodium persulfate dissolved in 884.9 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed composed of 1725.7 g of water, 121.0 g of AEROSOL 18 (35% solution in water), 48.2 g of TERGITOL NP-40 (70%), 2371.0 g of styrene, 1654.7 g of 2-ethylhexyl acrylate,
30 378.2 g of allyl methacrylate, 189.1 g of dimethylaminoethyl methacrylate, 40.2 g of 2-

ethylhexyl 3-mercaptopropionate, and 189.1 g of ROHAMERE 6852-0 (50% solution in water) was fed into the reactor over 71 minutes. After the last feed, the temperature was cooled to 65°C and a solution of 117.4 g of demineralized water, 27.0 g of sodium formaldehyde sulfoxylate, and 49.8 g of a 0.5% solution of iron (II) sulfate by seven
5 water (chelated with EDTA) was charged to the reactor. Then a solution 29.01 g of t-butylhydro-peroxide (70% in water) dissolved in 117.4 g of demineralized water was over 40.6 minutes while heating continued. The emulsion was cooled and pumped from the reactor. Solids Level, 48.08%; DSC reheat midpoint glass transition 15°C.

10 RESIN B

To a 5 gallon resin kettle equipped with a condenser, nitrogen purge, and above surface feed tube were added 4176.6 g of water, 57.6 g of sodium carbonate, 22.65 g of TREM LF-40 (40% solids in water), 10.82 g of TERGITOL NP-40 (70% solids in water), 138.3 g of methyl methacrylate, 228.4 g of styrene, 266.4 g of 2-ethylhexyl
15 acrylate, and 1.3 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an initiator charge composed of 60.8 g of sodium persulfate dissolved in 343.4 g of demineralized water were added to the reactor. An emulsified monomer mixture composed of 2597.7 g of water, 65.56 g of TREM LF-40, 57.2 g of TERGITOL NP-40,
20 849.5 g of methyl methacrylate, 1402.8 g of styrene, 1636.6 g of 2-ethylhexyl acrylate, and 7.8 g of trimethylolpropane triacrylate followed by 100 g line flush of demineralized water, was fed over 125 minutes. Five minutes after the emulsion feed was begun, an initiator solution composed of 34.3 g of sodium persulfate dissolved in 884.9 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed
25 composed of 1617.9 g of water, 121.0 g of AEROSOL 18 (35% solution in water), 48.2 g of TERGITOL NP-40 (70%), 2276.4 g of styrene, 1654.7 g of 2-ethylhexyl acrylate, 378.2 g of allyl methacrylate, 189.1 g of dimethylaminoethyl methacrylate, 40.2 g of 2-ethylhexyl 3-mercaptopropionate, 378.2 g of ROHAMERE 6852-0 (50% solution in water) and 13.2 g of 2-acrylamido-2-methylpropanesulfonate (50% in water) was fed into
30 the reactor over 71 minutes. After the last feed, the temperature was cooled to 65°C and

a solution of 117.4 g of demineralized water, 27.0 g of sodium formaldehyde sulfoxylate, 49.8 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) was charged to the reactor. Then a solution 29.01 g of t-butylhydroperoxide (70% in water) dissolved in 117.4 g of demineralized water was over 40.6 minutes while heating
5 continued. The emulsion was cooled and pumped from the reactor. Solids Level, 47.25%; DSC reheat midpoint glass transition 14°C.

RESIN C

To a 50 gallon reactor were added 41765.9 g of water, 575.5 g of sodium
10 carbonate, 226.6 g of TREM LF-40 (40% solids in water), 108.2 g of TERGITOL NP-40 (70% solids in water), 1382.8 g of methyl methacrylate, 2283.6 g of styrene, 2664.2 g of 2-ethylhexyl acrylate, and 12.7 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an initiator charge composed of 607.5 g of sodium persulfate dissolved in 3433.6
15 g of demineralized water were added to the reactor. An emulsified monomer mixture composed of 2597.7 g of water, 655.6 g of TREM LF-40, 572.1 g of TERGITOL NP-40, 8494.7 g of methyl methacrylate, 14027.8 g of styrene, 16365.9 g of 2-ethylhexyl acrylate, and 77.9 g of trimethylolpropane triacrylate followed by 1000 g line flush of demineralized water, was fed over 125 minutes. Five minutes after the emulsion feed
20 was begun, an initiator solution composed of 343.4 g of sodium persulfate dissolved in 8848.5 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed composed of 15178.5 g of water, 1210.1 g of AEROSOL 18 (35% solution in water), 481.6 g of TERGITOL NP-40 (70%), 22764.2 g of styrene, 16547.5 g of 2-ethylhexyl acrylate, 3782.2 g of allyl methacrylate, 1891.1 g of dimethylaminoethyl
25 methacrylate, 401.9 g of 2-ethylhexyl 3-mercaptopropionate, 3782.2 g of ROHAMER 6852-0 (50% solution in water) and 132.1 g of 2-acrylamido-2-methylpropanesulfonate (50% in water) triacrylate followed by 1000 g line flush of demineralized water, was fed into the reactor over 71 minutes. After the last feed, the temperature was cooled to 65°C and a solution of 1174.0 g of demineralized water, 269.6 g of sodium formaldehyde
30 sulfoxylate, 497.5 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with

EDTA) was charged to the reactor. Then a solution 290.1 g of t-butylhydroperoxide (70% in water) dissolved in 1174.0 g of demineralized water was over 40.6 minutes while heating continued. The emulsion was cooled and pumped from the reactor. Solids Level, 47.8%; DSC reheat midpoint glass transition 20°C.

5

RESIN D

To a 50 gallon reactor were added 37589.3 g of water, 518 g of sodium carbonate, 203.9 g of TREM LF-40 (40% solids in water), 97.4 g of TERGITOL NP-40 (70% solids in water), 1244.6 g of methyl methacrylate, 2055.3 g of styrene, 2397.8 g of 2-ethylhexyl acrylate, and 11.4 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an initiator charge composed of 546.7 g of sodium persulfate dissolved in 3090.2 g of demineralized water were added to the reactor. An emulsified monomer mixture composed of 23379.4 g of water, 590.0 g of TREM LF-40, 514.9 g of TERGITOL NP-40, 7645.2 g of methyl methacrylate, 12625.0 g of styrene, 14729.3 g of 2-ethylhexyl acrylate, and 70.14 g of trimethylolpropane triacrylate followed by 900 g line flush of demineralized water, was fed over 95 minutes. Five minutes after the emulsion feed was begun, an initiator solution composed of 309.0 g of sodium persulfate dissolved in 7963.7 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed composed of 13660.7 g of water, 1089.1 g of AEROSOL 18 (35% solution in water), 433.4 g of TERGITOL NP-40 (70%), 20487.8 g of styrene, 14892.7 g of 2-ethylhexyl acrylate, 3404.0 g of allyl methacrylate, 1702.0 g of dimethylaminoethyl methacrylate, 361.7 g of 2-ethylhexyl 3-mercaptopropionate, 3404.0 g of ROHAMERE 6852-0 (50% solution in water) and 118.8 g of 2-acrylamido-2-methylpropanesulfonate (50% in water) triacrylate followed by 900 g line flush of demineralized water, was fed into the reactor over 95 minutes. After the last feed, the temperature was cooled to 65°C and a solution of 1056.6 g of demineralized water, 242.7 g of sodium formaldehyde sulfoxylate, 447.8 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) was charged to the reactor. Then a solution 261.1 g of t-butylhydroperoxide (70% in water) dissolved in 1056.6 g of demineralized water was over 40.6 minutes while heating continued. The

30

emulsion was cooled and pumped from the reactor. Solids Level, 45.5%; DSC reheat midpoint glass transition 15°C.

RESIN E

5 To a 5 gallon resin kettle equipped with a condenser, nitrogen purge, and above surface feed tube were added 4176.6 g of water, 57.6 g of sodium carbonate, 22.65 g of TREM LF-40 (40% solids in water), 10.82 g of TERGITOL NP-40 (70% solids in water), 138.3 g of methyl methacrylate, 228.4 g of styrene, 266.4 g of 2-ethylhexyl acrylate, and 1.3 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then
10 the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an initiator charge composed of 60.8 g of sodium persulfate dissolved in 343.4 g of demineralized water were added to the reactor. An emulsified monomer mixture composed of 2597.7 g of water, 65.56 g of TREM LF-40, 57.2 g of TERGITOL NP-40, 849.5 g of methyl methacrylate, 1402.8 g of styrene, 1636.6 g of 2-ethylhexyl acrylate,
15 and 7.8 g of trimethylolpropane triacrylate followed by 100 g line flush of demineralized water, was fed over 125 minutes. Five minutes after the emulsion feed was begun, an initiator solution composed of 34.3 g of sodium persulfate dissolved in 884.9 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed composed of 1631.1 g of water, 121.0 g of AEROSOL 18 (35% solution in water), 48.2 g
20 of TERGITOL NP-40 (70%), 2276.4 g of styrene, 1654.7 g of 2-ethylhexyl acrylate, 378.2 g of allyl methacrylate, 189.1 g of dimethylaminoethyl methacrylate, 40.2 g of 2-ethylhexyl 3-mercaptopropionate, and 378.2 g of ROHAMERE 6852-0 (50% solution in water) was fed into the reactor over 71 minutes. After the last feed, the temperature was cooled to 65°C and a solution of 117.4 g of demineralized water, 27.0 g of sodium
25 formaldehyde sulfoxylate, 49.8 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) was charged to the reactor. Then a solution 29.01 g of t-butylhydroperoxide (70% in water) dissolved in 117.4 g of demineralized water was over 40.6 minutes while heating continued. The emulsion was cooled and pumped from the reactor. Solids Level, 46.9%.

RESIN F

To a 50 gallon reactor were added 40364.1 g of water, 503.8 g of sodium carbonate, 1151.61 g of HITENOL HS-20 (9.7% solution in water), 133.2 g of

5 TERGITOL NP-40 (70% solids in water), 431.9 g of methyl methacrylate, 714.4 g of styrene, 833.1 g of 2-ethylhexyl acrylate, and 4.0 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 125 rpm. After reaching 80°C, an initiator charge composed of 531.7 g of sodium persulfate dissolved in 3005.0 g of demineralized water were added to the reactor. An emulsified

10 monomer mixture composed of 23973.4 g of water, 237.4 g of AEROSOL OT-75 (75% solution in water), 705.4 g of TERGITOL NP-40, 8212.4 g of methyl methacrylate, 13562.1 g of styrene, 15823.9 g of 2-ethylhexyl acrylate, and 7.52 g of trimethylolpropane triacrylate followed by 899.7 g line flush of demineralized water, was fed over 95 minutes. Five minutes after the emulsion feed was begun, an initiator

15 solution composed of 300.5 g of sodium persulfate dissolved in 7744.6 g of deionized water was fed in over 255 minutes. After the flush, a second emulsion feed composed of 15334.5 g of water, 754.0 g of AEROSOL 18 (35% solution in water), 351.3 g of TERGITOL NP-40 (70%), 20347.6 g of styrene, 14202.6 g of 2-ethylhexyl acrylate, 3244.3 g of allyl methacrylate, 1619.5 g of dimethylaminoethyl methacrylate, 345.0 g of

20 2-ethylhexyl 3-mercaptopropionate, and 1622.2 g of ROHAMERE 6852-0 (50% solution in water) was fed into the reactor over 95 minutes. After the last feed, the temperature was cooled to 65°C and a solution of 1034.7 g of demineralized water, 236.0 g of sodium formaldehyde sulfoxylate, 435.4 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) was charged to the reactor. Then a solution 253.9 g of t-

25 butylhydroperoxide (70% in water) dissolved in 1034.7 g of demineralized water was over 40.6 minutes while heating continued. The emulsion was cooled and pumped from the reactor. Solids Level, 45.9%.

RESIN G

To a 3000 ml resin kettle equipped with a condenser, nitrogen purge, and subsurface feed tube were added 480 g of water, 1.296 g of HITENOL HS-20, 1.59 g of TERGITOL 15-S-40 (68%), 5.8 g of sodium carbonate, 4.85 g of methyl methacrylate, 5 7.8 g of styrene, 9.86 g of 2-ethylhexyl acrylate, and 0.23 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 400 rpm. After reaching 80°C, an initiator charge composed of 6.164 g of sodium persulfate dissolved in 34.84 g of deionized water were added to the reactor. An emulsion feed at 5.248 g/minute composed of 208 g of water, 2.752 g of AEROSOL OT- 10 75, 8.408 g of TERGITOL 15-S-40 (68%), 92.16 g of methyl methacrylate, 148.50 g of styrene, 187.37 g of 2-ethylhexyl acrylate, and 4.37 g of trimethylolpropane triacrylate was begun. Five minutes after the first emulsion feed was begun, an initiator solution composed of 3.48 g of sodium persulfate dissolved in 89.78 g of deionized water was fed in at 0.336 g/min. After the first emulsion feed was completed, 64 g of water was fed 15 through the monomer feed line at 52.48 g/minute and the reactor was held at temperature for 25 minutes. After the hold, a second emulsion feed composed of 138 g of water, 8.74 g of AEROSOL 18, 4.22 g of TERGITOL 15-S-40 (70%), 203.52 g of styrene, 172.71 g of 2-ethylhexyl acrylate, 2.77 g of 2-ethylhexyl 3-mercaptopropionate, 95.95 g of acetoacetyl methacrylate, and 4.80 g of 2-acrylamido-2-methylpropanesulfonate (50% in 20 water) was fed into the reactor at 8 g/min. Ten minutes after the last feed, the temperature was cooled to 65°C and a solution of 0.8 g of isoascorbic acid in 16 g of water and 1.6 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) in water was charged to the reactor. Then an initiator solution of 1.04 g of t-butylhydroperoxide (70% in water) dissolved in 16 g of water was fed at 0.38 g/min. 25 while heating continued. The emulsion was cooled then filtered through 100 mesh wire screen. Solids Level, 47.1%.

RESIN H

To a 3000 ml resin kettle equipped with a condenser, nitrogen purge, and 30 subsurface feed tube were added 720.4 g of water, 39.2 g of HITENOL HS-20, 1.08 g of

TERGITOL 15-S-40 (68%), 5.8 g of sodium carbonate, 25.52 g of methyl methacrylate, 35.2 g of styrene, 26.4 g of 2-ethylhexyl acrylate, and 0.88 g of trimethylolpropane triacrylate. A nitrogen purge was begun, then the contents of the reactor brought up to 80°C at 400 rpm. After reaching 80°C, an initiator charge composed of 6.032 g of sodium persulfate dissolved in 34.84 g of deionized water were added to the reactor. An emulsion feed at 5.248 g/minute composed of 158.4 g of water, 15.72 g of AEROSOL OT-75, 11.004 g of TERGITOL 15-S-40 (68%), 107.81 g of methyl methacrylate, 148.70 g of styrene, 111.53 g of 2-ethylhexyl acrylate, and 3.72 g of trimethylolpropane triacrylate was begun. Five minutes after the first emulsion feed was begun, an initiator solution composed of 3.41 g of sodium persulfate dissolved in 87.2 g of deionized water was fed in at 0.336 g/min. After the first emulsion feed was completed, 60 g of water was fed through the monomer feed line at 52.48 g/minute and the reactor was held at temperature for 25 minutes. After the hold, a second emulsion feed composed of 138.4 g of water, 9.72 g of AEROSOL 18, 6.99 g of TERGITOL 15-S-40 (70%), 191.90 g of styrene, 43.25 g of methyl methacrylate, 143.93 g of 2-ethylhexyl acrylate, 95.95 g of acetoacetyl methacrylate, and 9.448 g of 2-acrylamido-2-methylpropanesulfonate (50% in water) was fed into the reactor at 5.248 g/min. Ten minutes after the last feed, the temperature was cooled to 65°C and a solution of 1.04 g of isoascorbic acid in 16 g of water and 1.6 g of a 0.5% solution of iron (II) sulfate by seven water (chelated with EDTA) in water was charged to the reactor. Then an initiator solution of 1.04 g of t-butylhydroperoxide (70% in water) dissolved in 16 g of water was fed at 0.38 g/min. while heating continued. The emulsion was cooled to less than 35°C then filtered through 100 mesh wire screen. Solids Level, 47.1%.

25 RESIN I

To 752.0 g of Resin H was added 56.1 g of a 50% solution of POLYMIN-G in water with stirring.

RESIN J

This resin blend was prepared by adding 556.5 g of Resin G to a glass resin kettle. At ambient temperature with stirring, first 199.5 g of Resin I, then 10.5 g of 0.3 molar solution of ammonium carbonate in water was added.

5

EXAMPLE 1

SURFYNOL® 104 was added to Resin A as shown in Table 1 below at increasing percentage levels based on weight of surfactant per weight of resin solid. SURFYNOL® 104 is a solid at room temperature and had to be warmed to 140°F to
 10 liquefy before adding to the latex. The depression in both minimum film forming temperature (MFFT) and glass transition (Tg) are characteristic of plasticization behavior.

Table 1: Minimum Film Forming Temperature (visual) and Glass Transition (Tg °C)
Measurements of Latex Resin at increasing levels of SURFYNOL® 104:

15	%	0	1	2	3	4
	MFFT (°C)	14.	11	114	9.3	8.7
	Tg Midpoint	14.	129	11	8.4	7.2

20

EXAMPLE 2

SURFYNOL® 104 or 420 was added to Resin B as shown in Table 2 below at 3.4% weight of surfactant solid per weight of resin solid. The depression in the onset and midpoint Tg °C of the samples with either SURFYNOL® versus the neat resin is indicative of plasticization behavior.

Table 2: Onset/midpoint Glass Transition (Tg°C) measurements on Four Latex Resins with and without SURFYNOL®104 or 420 added:

Latex Sample	Tg°C ^{*/} without surfactant	Tg°C* with SURFYNOL® 104	Tg°C* with SURFYNOL® 420
RESIN B	6/15	1/9	2/9
RESIN C	9/18	3/11	-3/8
RESIN D	7/16	-1/8	3/10
RESIN E	5/13	-3/5	-1/7

10 **EXAMPLE 3**

Plasticization can also be demonstrated using tensile properties of emulsion films. As shown in Table 3 below, when SURFYNOL® 104 was added to Resin A (3.4% weight of surfactant solid per weight of resin solid) there was a reduction in break, work and modulus along with an increase in elongation. This is typical of a change in

15 performance observed in a plasticized film.

Table 3: Tensile properties of Clear Resin A film with and without SURFYNOL®104:

Sample	Ultimate Break (psi)	Ultimate Elongation (%)	Work	Initial Modulus (ksi)
- surfactant	1106	370	1841	7.8
+ surfactant	780	536	1318	0.7

20

EXAMPLE 4

In this Example a low VOC glossy latex coating (<11 g/l) was prepared with and without surfactant.

Preparation of Zero Volatile Organic Compound (VOC) Grind:

25 A 15 gallon grind (Grind 1) was prepared using a Premier disperser, as below, and a portion of the grind was used to letdown each specified paint.

* / onset/midpoint

Material:	Volume (gallons):
Water	48.00
TAMOL 1124	4.00
TRITON CF-10	2.00
5 FOAMASTER AP	2.00
DOWICIL 75	1.00

Disperse well then add under agitation:

TI-PURE R-900	200.00
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10

The batch was dispersed at high speed until the dispersion passed 7 on a Hegman gauge, then 19 lb of water was added. The bath was then filtered through a Fulflo filter and stored.

15 Preparation of Aqueous Latex Coatings at 18 Pigment Volume Concentration (PVC):

The following four paint letdowns were prepared using the Zero VOC grind (above) and emulsions shown.

Paint Letdown (weight in g):

20 Paint Sample (see Table 4):	1	2	3	4
<i>Material:</i>				
Zero VOC Grind 1	490	140	140	140
Resin B	819	234	234	234
25 FOAMASTER AP) Premix	7.2	1.0	1.0	1.0
FOAMASTER VF)	10.9	1.5	1.5	1.5
HYDROCURE II)	15.9	2.2	2.2	2.2
SURFYNOL 104A)	--	1.3	2.6	3.9
Water	210	56	58	59
30 <i>Then add:</i>				
ACRYSOL RM-5 Solution	182	52	52	52
<i>Then add:</i>				
CELLOSIZ 4400H Solution	35	10	11.2	11.2

Then adjust pH to 8.3 to 8.7 using 28% ammonia below:

NH₄OH 0.83 3.2 3.2 3.2

Table 4: Coating Formulations of Example 4 with and without Surfactant

5	Sample	Level
	1	0
	2	1.1
	3	2.3
	4	3.4

10

Table 5: Gloss, Low Temperature Coalescence, Stain and Scrub Properties of Coating Formulations of Example 4 with and without Surfactant:

15	Sample	60° Gloss	20° Gloss	Low Temperature Coalescence	Total Stain	8 day Scrub	15 day Scrub	21 day Scrub
	1	65	22	Failed	37	78	71	98
	2	75	40	Failed	31	73	115	84
	3	77	42	Failed	33	86	101	84
	4	79	41	Passed -2 Opacity	34	75	99	58

20

Table 6: Break Through and Total Failure Wet Adhesion Properties of Coating Formulations with and without Surfactant:

25	Sample	1 Day Wet Adhesion: Break Through/Total Failure	8 Day Wet Adhesion: BT/TF	15 Day Wet Adhesion: BT/TF	21 Day Wet Adhesion: BT/TF
	1	57/151	142/516	200/549	544/2081
	2	45/118	163/661	107/593	259/1126
	3	41/130	239/816	169/848	369/1214
	4	38/151	100/344	166/514	1210/2925

Table 7a: Block Resistance Properties of Coating Formulations with and without Surfactant:

5

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
1	6	7	7	9	3	3	6	8
2	6	5	7	8	2	3	9	9
3	8	4	7	9	1	3	6	9
4	4	4	5	8	1	3	8	6

Table 7b: Wet Block Resistance Properties of Coating Formulations with and without Surfactant:

15

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
1	0	1	0	5	0	0	0	4
2	0	1	0	0	1	0	0	2
3	0	0	0	1	0	0	0	2
4	0	1	0	3	0	0	0	1

Table 7c: Print Resistance Properties of Coating Formulations with and without Surfactant:

25

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
1	4	4	6	8	4	6	6	6
2	6	6	6	6	2	8	8	8
3	6	4	6	8	2	8	8	6
4	6	4	4	8	4	6	8	6

35

Table 7d: Heated Block and Print Resistance Properties of Coating Formulations of Example 4 With and Without Surfactant:

5	Sample	ASTM Heated Block	ASTM Heated Block
	1	8	8
	2	4	8
	3	7	8
	4	4	8

10

EXAMPLE 5

In this example low VOC satin latex coatings (<11 g/l) with and without surfactant were prepared.

Preparation of Calcium Carbonate Grind:

15

Material: Weight (g):

Water 100

TAMOL 1124 8.0

20 TRITON CF-10 4.0

FOAMASTER AP 30.0

DOWICIL 75 10.0

Mix well at high speed for 5 minutes

25 OMYACARB UF 400.0

Water 24.0

Disperse high speed for 15 minutes:

Water 50

30

35

Letdown of Satin Coatings:

	<u>Sample 5:</u>	<u>Sample 6:</u>
Calcium Carbonate Grind	30.1	30.1
5 <i>Add slowly under agitation</i>		
RESIN F	220.2	220.2
R-746 TiO ₂ Slurry	83.0	83.0
Ropaque OP-62LO	50.0	50.0
Water	77.0	77.0
10		

Premix:

	SURFYNOL 420	--	3.45
	FOAMASTER AP	--	1.15
15	FOAMASTER VF	--	1.0
	5% Cobalt HYDROCURE II	--	2.0
	TAFIGEL PUR 45 Solution	10.0	10.0

Adjust Viscosity to 85 KU +/-3 with the following:

20	RHEOVIS CR2 Solution	20.0	20.0
	Ammonia (28%)	0.5	0.5

Table 8: Satin Coating Formulations With and Without Surfactant:

25	Sample	Level
	5	0
	6	3.8

Table 9: Gloss, Low Temperature Coalescence, Stain and Scrub Properties of Coating Formulations with and without Surfactant:

Sample	60°Gloss	20°Gloss	Low Temperature Coalescence	Total Stain	8 day Scrub	15 day Scrub	21 day Scrub
5	36	7	Failed	32	354	660	629
6	45	9	Passed, -2 Opacity	31	758	814	873

Table 10: Break Through and Total Failure Wet Adhesion Properties of Coating Formulations with and without Surfactant:

Sample:	1 Day Wet Adhesion: Break Through/Total Failure	8 Day Wet Adhesion: BT/TF	15 Day Wet Adhesion: BT/TF	21 Day Wet Adhesion: BT/TF
5	1058/3000+	3000+/3000+	1827/3000+	3000+/3000+
6	1660/3000+	3000+/3000+	2223/3000+	3000+/3000+

Table 11a: Block Resistance Properties of Coating Formulations with and without Surfactant:

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
5	8	6	7	6	6	5	7	6
6	4	4	8	7	5	4	7	7

Table 11b: Wet Block Resistance Properties of Coating Formulations with and without Surfactant:

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
5	1	6	6	6	1	3	6	5
6	0	5	5	6	1	2	6	6

Table 11c: Print Resistance Properties of Coating Formulations with and without Surfactant:

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
5	4	6	6	8	4	6	8	8
6	0	4	4	8	2	4	6	6

Table 11d: Heated Block and Print Resistance Properties of Coating Formulations with and without Surfactant:

5	Sample	ASTM Heated Block	ASTM Heated Print
	5	7	8
	6	6	8

Examples 4 and 5 demonstrate that the addition of SURFYNOL® 104 or 420 at 3.6% or higher on resin nonvolatile content to very low VOC paints (11 g/l calculated) resulted in the following balance of paint properties; pass low temperature coalescence (Tables 5 and 9), improved scrub resistance (Table 5 and 9), and higher gloss with no significant loss in block, print, wet adhesion or stain resistance properties (Tables 5-11).

15 **EXAMPLE 6**

In this Example a coating composition containing SURFYNOL® 420 at 5.6% was compared on containing cosolvent blend Eastman EB Solvent/Eastman DB Solvent. The substitution of SURFYNOL® 420 at 5.6% on resin nonvolatile content to make a very low VOC paint (less than 25 g/l VOC) in sample 8 for a cosolvent-containing paint (Eastman EB Solvent/Eastman DB Solvent at 100 g/l VOC) found in sample 7 resulted in the following balance of paint properties; sample 8 passes low temperature coalescence over a range of relative humidities whereas sample 7 does not (Table 13), and equivalent scrub resistance (Table 14), block resistance, print resistance, and wet adhesion (Tables 14, 15 and 16).

25

Preparation of Grind:

A 15 gallon grind was prepared using a Premier disperser, as below, and a portion of the grind was used to letdown each specified paint.

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30

Material:**Weight (g):**

	10% solution of ammonium carbonate in water:	200
	PROXEL GXL	2.6
5	TAMOL 1124	10.4
	TRITON CF-10	5.2
	FOAMASTER AP	6.0
	DURAMITE	320.0
	NYTAL 300	200.0
10	Disperse well.	

Preparation of PREMIX 1:

15	Eastman EB Solvent	15.0
	Eastman DB Solvent	15.0
	FOAMASTER AP	6.7
	FOAMASTER VF	3.2
20	AEROSOL OT-75	1.0

Preparation of PREMIX 2:

	SURFYNOL®420	11.2
25	FOAMASTER AP	6.7
	FOAMASTER VF	3.2
	AEROSOL OT-75	1.0

Preparation of Satin Latex Coatings:

30 The following two paint letdowns were prepared using the grind (above) and emulsions shown.

Paint Letdown (weight in g):

35	Paint Sample (see Table 8):	7	8
	<i>Material:</i>		
	Grind	83.0	83.0
40	RESIN J	217.5	217.5
	TIPURE R-746 Slurry	124.0	124.0
	Premix 1	20.5	--
	Premix 2	--	11.0
	Deionized Water	23.5	33.0
45	TAFIGEL PUR 45 Solution	15.2	15.0

Adjust viscosity to 89 (+/- 3) KU with the following:

CR2 Solution	14.0	15.0
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5 Then adjust pH to 8.7 to 9.1 using 0.3 molar ammonium carbonate:

$(\text{NH}_4)_2\text{CO}_3$	0.0	1.0
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Satin Coating Formulations on Resin J with SURFYNOL® 420 or cosolvents:

10 Table 12: Coating Formulations with coalescent or with surfactant

Sample	SURFYNOL ® 420 Level	Eastman EB/ Eastman DB Level	85/60/20° Gloss
7	0	7.3/7.3	18/18/3
8	5.6	0	16/15/3

Table 13. Low Temperature Coalescence with Coalescent or Surfactant:

Sample	Low Temperature Coalescence: 50% Relative Humidity and 40°F	Low Temperature Coalescence: 50% Relative Humidity and 40°F	Low Temperature Coalescence: 50% Relative Humidity and 40°F
7	Failed	Failed	Failed
8	Passed	Passed	Passed

Table 14: Break Through Wet Adhesion and Scrub Resistance Properties of

25 Coating Formulations with and without Surfactant:

Sample	1 Day Wet Adhesion Break Through	8 Day Scrub Resistance	15 Day Scrub Resistance	21 Day Scrub Resistance
7	3000	1000	1409	1885
8	3000	1000	1238	1952

Table 15: Block Resistance Properties of Coating Formulations with and without Surfactant:

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
7	4	6	--	8	6	7	--	10
8	8	8	--	10	7	8	--	10

Table 16: Print Resistance Properties of Coating Formulations with and without Surfactant:

Sample	One day Face-to-Face Block Resistance				Seven day Face-to-Face Block Resistance			
	1 day dry	2 day dry	7 day dry	21 day dry	1 day dry	2 day dry	7 day dry	21 day dry
7	8	8	--	10	8	8	--	8
8	8	8	--	10	8	8	--	8

The above examples demonstrate that surfactants function as a plasticizers in the coating, thus eliminating the need for conventional cosolvents and eliminate the VOC's associated with the cosolvents. Preferably, according to the invention, surfactants function to plasticize a coating, aid in low temperature film formation and contribute to the typical properties not previously known for surfactants in coatings while not contributing deleteriously to the final balance of properties in the finished coating.

We Claim:

1. A water-based polymer coating composition comprising a polymer resin, water and surfactant, the improvement wherein:

(A) the surfactant is present in an amount effective to plasticize a coating formed from the composition, and wherein the surfactant is an anionic surfactant, a nonionic surfactant or a mixture thereof; and

(B) the coating composition is substantially free from co-solvents.

2. A water-based polymer coating composition according to Claim 1, wherein the surfactant is an anionic surfactant selected from alkali metal or ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates.

3. A water-based polymer coating composition according to Claim 2, wherein the surfactant is selected from alkali metal or ammonium salts of lauryl sulfate, octylphenol glycol ether sulfate, dodecylbenzene sulfonate, lauryldiglycol sulfate, tritertiarybutyl phenol sulfonate, penta-glycol sulfonate, octa-glycol sulfonate, sulfosuccinate, and mixtures thereof.

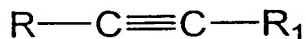
4. A water-based polymer coating composition according to Claim 1, wherein the nonionic surfactant is a polyether nonionic surfactant.

5. A water-based polymer coating composition according to Claim 4, wherein the polyether nonionic surfactant is an alkyl polyglycol ether, an alkyl phenol polyglycol ether or a mixture thereof.

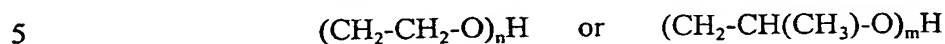
6. A water-based polymer coating composition according to Claim 5, wherein the alkyl phenol polyglycol ether is an ethoxylation product of octylphenol, nonylphenol, diisopropyl phenol, triisopropyl phenol or a mixture thereof.

7. A water-based polymer composition according to Claim 5, wherein the alkyl polyglycol ether is an ethoxylation product of a lauryl alcohol, an oleyl alcohol, a stearyl alcohol or mixtures thereof.

8. A water-based polymer coating composition according to Claim 5, wherein the alkyl polyglycol ether is selected from compounds of the formula:



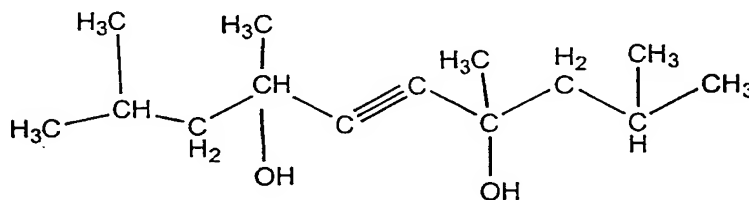
wherein R and R₁ are each selected from straight and branched alkyls having from 1 to 15 carbon atoms and wherein at least one of R and R₁ contains from 1 to 3 hydroxyl groups, and the H of each hydroxyl group is independently unsubstituted or substituted with a substituent of the formula



wherein n and m each range from 1 to about 50 and wherein the total of n and m is less than about 60.

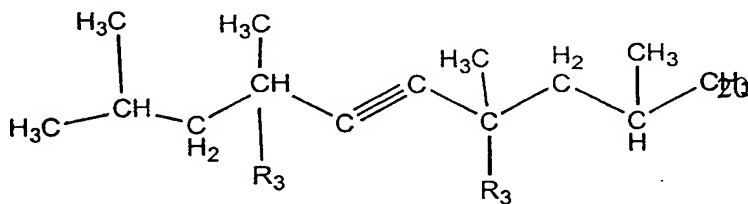
9. A water-based polymer coating composition according to Claim 8, wherein the alkyl polyglycol ether is a compound of the formula:

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15

10. A water-based polymer coating composition according to Claim 8, wherein the alkyl polyglycol ether is selected from compounds of the formula:



wherein R₃ is $(\text{CH}_2-\text{CH}_2-\text{O})_n\text{H}$ and wherein n is a number ranging from 1 to 30.

11. A water-based polymer coating composition according to Claim 10, wherein n is
- 25 1.3.
12. A water-based polymer coating composition according to Claim 10, wherein n is
- 3.5.
13. A water-based polymer coating composition according to Claim 10, wherein n is
- 10.

14. A water-based polymer coating composition according to Claim 10, wherein n is 30.

15. A water-based polymer coating composition according to Claim 1, further comprising an additive selected from a solvent, a pigment, a leveling agent, a rheology agent, a flow control agent, an extender, a reactive coalescing aid, a flattening agent, a pigment wetting agent, a dispersing agent, a surfactant, an ultraviolet (UV) absorber, a UV light stabilizer, a defoaming agent, an antifoaming agent, an anti-settling agent, an anti-sag agent, a bodying agent, an anti-skinning agent, an anti-flooding agent, an anti-floating agent, a fungicide, a mildewcide, a corrosion inhibitor, a thickening agent, a plasticizer, a reactive plasticizer, a curing agent, a coalescing agent, and mixtures thereof.

16. A water-based polymer coating composition according to Claim 1, having a VOC of less than 250 g/l.

17. A water-based polymer coating composition according to Claim 16, having a VOC of less than 50 g/l.

18. A substrate coated with a composition according to Claim 1.

19. The substrate of Claim 18, wherein the substrate is selected from wood, wood by-products, gypsum board, plastic, metal, and textile products.

20. A process of coating a substrate comprising the steps of coating the substrate with a water-based polymer coating composition according to Claim 1 and allowing the coating to cure.

21. A process according to Claim 20, wherein the substrate is selected from wood, wood by-products, gypsum board, plastic, metal, and textile products.

22. A water-based polymer coating composition according to Claim 1, wherein the surfactant is present in an amount ranging from about 3% to about 10% by weight of dry polymer.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/16859

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09D5/02 C09D7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 234 394 A (BP CHEMICALS) 3 June 1971 see claims	1,4-7, 15-22
X	EP 0 655 495 A (AIR PRODUCTS AND CHEMICALS) 31 May 1995 see page 3, line 10-36 see page 4, line 1-10; example 1	1,4,5,8, 10-21

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1234394 A	03-06-1971	NONE	
EP 655495 A	31-05-1995	CA 2136373 A	30-05-1995
		JP 7188087 A	25-07-1995
		US 5650543 A	22-07-1997

